

Sulphur, oxygen and strontium isotope compositions of Middle Miocene (Badenian) calcium sulphates from the Carpathian Foredeep, Poland: palaeoenvironmental implications

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Sulphur, oxygen and strontium isotope compositions have been measured in sulphate (gypsum and anhydrite) samples from the Badenian evaporite complex in the Carpathian Foredeep Basin (Poland) to determine the origin of brines from which these sulphates were formed. Studied samples display the δ values from +22.68 to +24.91‰ CDT for sulphur (ten samples) and from +12.26 to +13.63‰ SMOW for oxygen (ten samples), and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from 0.708915 to 0.716329 (six samples). Most samples show isotopic values (both $\delta^{34}\text{S}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) higher than contemporaneous (Badenian) seawater, and thus suggest that these sulphates were formed (i) from brines with a significant component of non-marine waters, (ii) in a restricted system, where an important role was played by meteoric water inputs as well as by bacterial sulphate reduction. The results of this study show clear differences in the isotopic signatures between sedimentary (gypsum) and diagenetic (anhydrite) lithofacies. While sedimentary gypsum displays sulphur, oxygen and strontium isotope ratios close to contemporaneous (Badenian) seawater, diagenetic anhydrite values are largely elevated. The higher isotopic values ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) for anhydrite when compared to gypsum are interpreted as reflecting different hydrological provenances of sulphate in the Badenian basin. Gypsum was formed from brines marine in origin that were subject to an important inflow of continental waters and a local bacterial sulphate reduction in a restricted, and therefore sulphate-limited basin, which is consistent with earlier interpretations based on sedimentological and geochemical studies. Our study shows that brines from which anhydrite was formed had a highly-radiogenic non-marine (riverine, groundwater) strontium component, which is a new contribution to the knowledge on the Badenian sulphate formation. The results reflect a lateral compositional evolution of parent waters during sulphate deposition and diagenesis in the Carpathian Foredeep Basin.

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Key words: Carpathian Foredeep; Badenian; sulphur, oxygen and strontium isotopes; sulphate deposits.

INTRODUCTION

Isotopic compositions ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$) and $^{87}\text{Sr}/^{86}\text{Sr}$ of sulphate deposits provide useful information about the origin and diagenetic evolution of the source waters (e.g., Schreiber and El Tabakh, 2000; Lu *et al.*, 2001; Palmer *et al.*, 2004). Interpretation of these data is, however, complex due to the restricted nature of depositional settings and the brine interactions upon deposition, which obscures the composition of mother brines (Denison *et al.*, 1998; Kah *et al.*, 2001; Lu and Meyers, 2003).

Thus, many ancient sulphate deposits interpreted as marine in origin may actually have a more complex origin, inasmuch as it is commonly difficult to differentiate evaporites deposited from marine water, non-marine water, or their mixtures (Hardie, 1984; Horita *et al.*, 2002; Palmer *et al.*, 2004).

The Middle Miocene Badenian sulphate deposits in the Carpathian Foredeep (Poland) (Fig. 1) have been conventionally described as formed in a marine basin. This interpretation has been confirmed by the sulphur and oxygen isotope composition of sulphates (e.g., Hałas *et al.*, 1996; Kasprzyk, 1997; Peryt *et al.*, 1998; Rosell *et al.*, 1998). Recently Cendón *et al.* (2004) argued, based on geochemical data (fluid inclusion

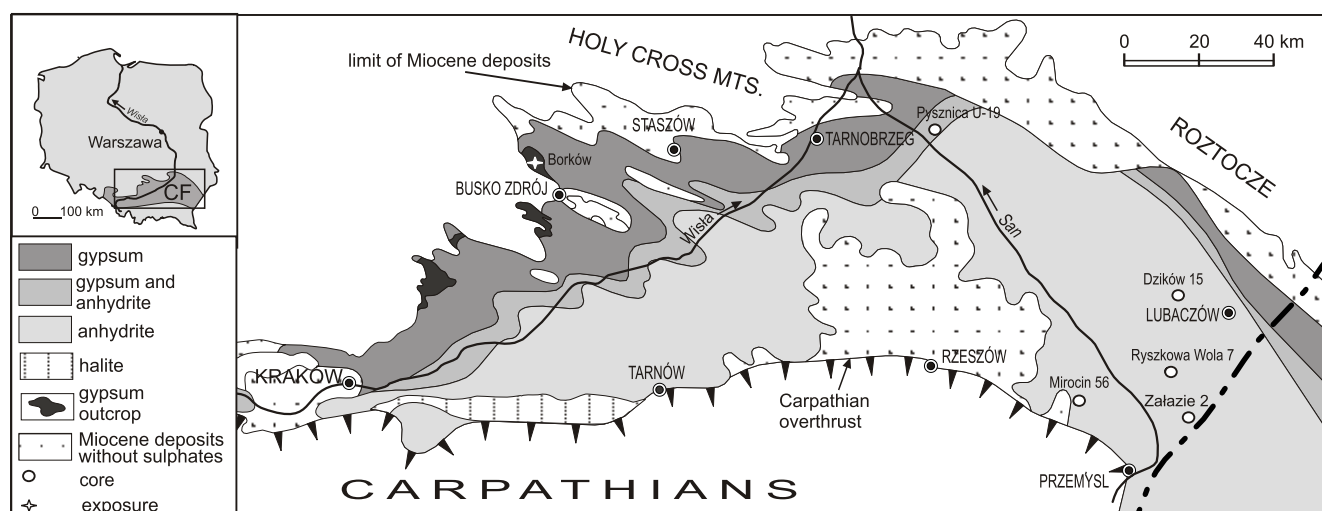


Fig. 1. Distribution of Badenian sulphate facies in the Carpathian Foredeep of Poland

composition and Br content in halite) and geochemical modelling, that the brine composition in the Badenian basin might have been strongly modified by freshwater inflows and intrabasinal recycling of previously formed evaporites during the evaporite deposition.

The Badenian sulphate deposits in the Carpathian Foredeep basin have not been studied previously for their Sr isotope geochemistry. In this paper the first Sr isotope data are presented and compared with those of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$, which permits to record the non-marine contribution to the basin, and to better constrain the origin and formation of these deposits.

SULPHATE FACIES DISTRIBUTION

Middle Miocene Badenian evaporites occupy a large part of the Carpathian Foredeep, that developed as a peripheral foreland basin in front of the Carpathian thrust advancing northwards (Oszczypko *et al.*, 2005) (Fig. 1). In the Polish part of the foredeep, these evaporites correspond to the lower part of the NN6 zone, thus they are late Badenian in age, based on the recent nannoplankton study and the radiogenic dating of the tuff horizon (Andreyeva-Grigorovich *et al.*, 2003; Dudek *et al.*, 2004), although traditionally they have been related to Wielician, i.e. middle Badenian. Evaporites are underlain and overlain by deep-water marine, mainly siliciclastic deposits, and comprise sulphate and halite facies with associated siliciclastic and carbonate deposits. The present-day extent of evaporites apparently represents only a part of the broader depositional succession, because most of the marginal facies are allochthonous or have not been preserved.

The Badenian sulphate deposits are widespread and correlate over a large area (17500 km²) in the Carpathian Foredeep of Poland (Fig. 1) and they continue further towards SE to Ukraine, Moldova, Romania and Bulgaria. In Poland sulphate deposits form a marginal platform that passes southward to the sulphate basin, while the axial part of the foredeep is occu-

pied by local salt basins. They show a regular lateral distribution of facies:

1. In the peripheral part of the foredeep the dominant sulphate facies, both in outcrop and in shallow subsurface, is up to 60 m thick primary gypsum filling the peripheral troughs (Kubica, 1992; Kasprzyk, 1993). The primary gypsum deposits display a wide variety of lithofacies. Two gypsum members are distinguished (Fig. 2): a lower member of mostly autochthonous, selenitic facies, and an upper member composed mainly of allochthonous, clastic deposits (Kasprzyk, 1999; Bąbel, 1999).
2. Towards the south, in more buried parts of the basin, gypsum is replaced by anhydrite (now in near-surface as secondary gypsum). A vertical succession of lithofacies comprises nodular and massive anhydrite with pseudomorphs after selenitic gypsum in the lower part (Kasprzyk, 2003). This lower part correlates with the lower (selenitic, autochthonous) gypsum member and are overlain by laminated anhydrite and breccias, widely distributed in the foredeep, which are equivalent to the upper (clastic, allochthonous) gypsum member (Kasprzyk and Ortí, 1998) (Fig. 2). In the southern part of the foredeep these anhydrite deposits are up to 20 m thick and change laterally into basin centre sulphate laminites and halite deposits (Garlicki, 1979).

The preservation of pseudomorphic features inherited from the precursor gypsum rocks, both selenitic (lower member) and clastic (upper member), provides important evidence for diagenetic anhydrite formation by replacement of the former gypsum during early to late diagenesis (Kasprzyk and Ortí, 1998; Kasprzyk, 2003, 2005). Kasprzyk and Ortí (1998) distinguished two different genetic patterns of anhydrite: (i) syndepositional to early-diagenetic anhydritization of gypsum deposits in surficial to shallow-burial environments (lower member), and (ii) several phases (syndepositional de novo growth, early diagenetic to late diagenetic replacement of former gypsum) of anhydrite formation during progressive burial (upper member). All genetic types of Badenian anhydrite display particular sedimentological and petrographic features recently described in details by Kasprzyk (2003, 2005), and two

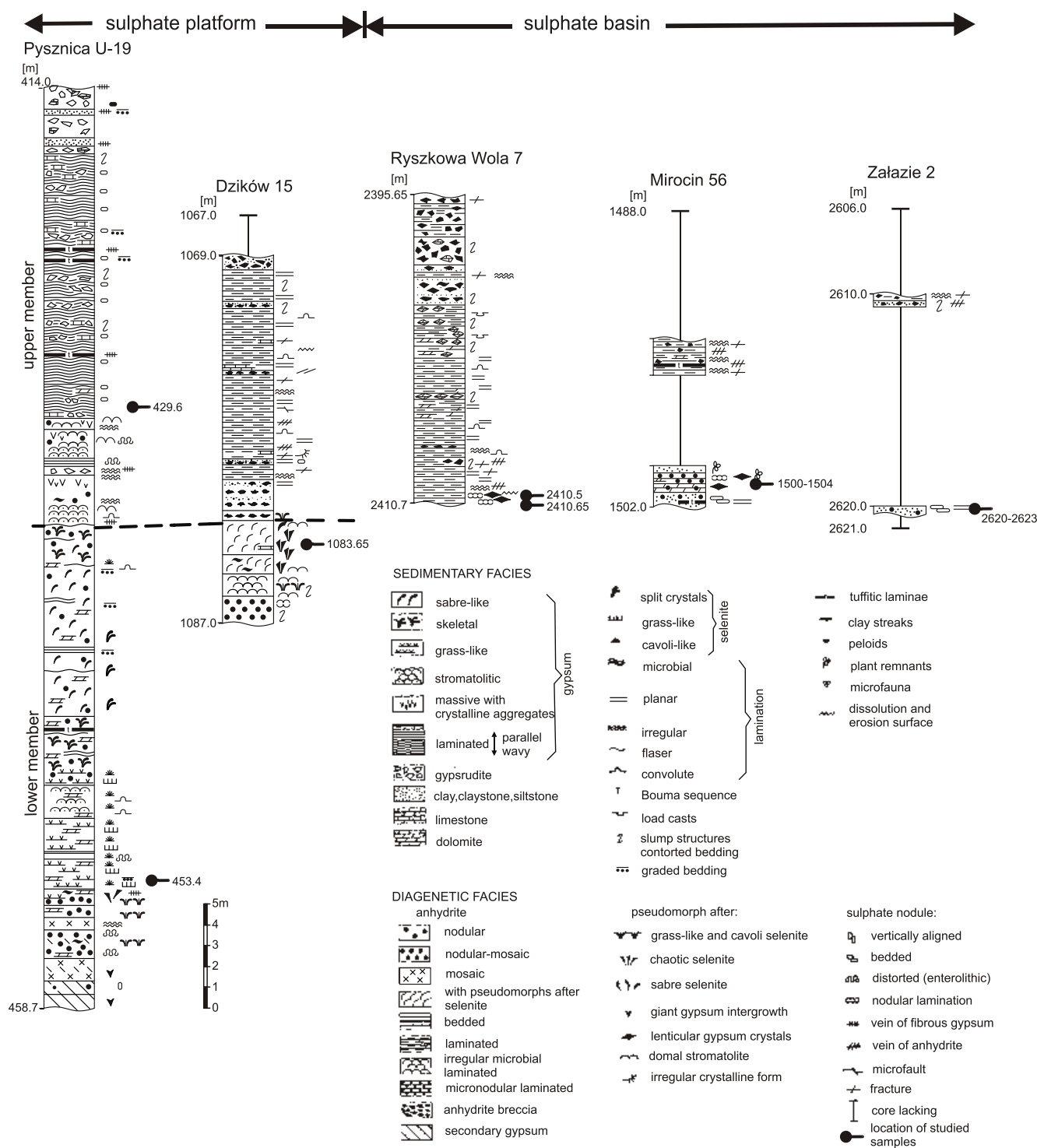


Fig. 2. Badenian sulphate successions representative of various settings, and locations of studied samples

of these types have been considered for purposes of this study. Syndepositional anhydrite of the lower member (samples no. 4 and 6 in Table 1) is characterized by the nodular fabrics and pseudomorphous replacement growth. Early diagenetic anhydrite of the upper member (samples no. 7–10 in Table 1) display features of displacement formation in a soft, only partly lithified sediment (Kasprzyk, 2005). In some areas, shallow

burial and/or uplift and exhumation have allowed the anhydrite to be partly or completely rehydrated into secondary gypsum.

Deposition of Badenian evaporites in the Carpathian Foredeep of Poland took place in a restricted basin, as a response to sea level fall (Oszczypko *et al.*, 2005; Peryt, 2006), and was controlled by climatic and tectonic changes which affected the interplay between inflow, reflux and evaporation in

Table 1

O, S and Sr isotope data of Badenian sulphate samples

No.	Borehole/Exposure	Depth [m]/sample	Lithofacies/Member I — lower, II — upper	Isotope composition		
				$\delta^{18}\text{O}_{\text{‰SMOW}}$	$\delta^{34}\text{S}_{\text{‰CDT}}$	$^{87}\text{Sr}/^{86}\text{Sr}$
1	Pysznica U-19 (sulphate platform)	429.6	laminated clastic gypsum/II	12.68	22.91	0.708915
2		429.6	laminated clastic gypsum/II	12.94	22.07	n.a.
3		453.4	selenitic gypsum/I	12.26	22.68	0.709157
4		453.4	anhydrite nodule within selenitic gypsum/I	13.63	24.52	0.709581
5	Borków (sulphate platform)	surface exposure	microbial laminated gypsum/I	12.49	23.15	n.a.
6	Dzików 15 (sulphate platform)	1083.65	anhydrite pseudomorph after selenitic gypsum/I	11.96	23.23	n.a.
7	Załawie 2 (sulphate basin)	2620–2623/4-G	laminated anhydrite/II	13.27	24.40	0.715231
8	Mirocin 56 (sulphate basin)	1500–1504/4-G	laminated anhydrite — anhydrite pseudo- morphs after lenticular gypsum crystals/II	12.36	24.47	0.710247
9	Ryszkowa Wola 7 (sulphate basin)	2410.5	laminated anhydrite — anhydrite pseudo- morphs after lenticular gypsum crystals/II	12.86	24.91	0.716329
10		2410.65	laminated anhydrite with pyrite/II	12.91	23.95	n.a.
x =				12.74	23.63	0.711577
SD =				0.39	0.82	0.002802

n.a. — not analysed, x — mean, SD — standard deviation

this marine-fed basin. The lateral and vertical facies distribution, the presence of detrital sulphate facies and the replacement of gypsum by anhydrite are a consequence of drops in the brine level linked to the basin restriction and to changes in the basin hydrology which were controlled by the evolution of the Carpathian orogen.

SAMPLE MATERIALS AND METHODS

The studied samples came from five boreholes located in the eastern part of the Carpathian Foredeep in Poland and intersecting the Badenian sulphate deposits at various depths (from 414.0 to 2621.0 m), and from one surface exposure (Borków quarry) in the northern peripheral part of the Carpathian Foredeep (Fig. 1). Isotopic analyses were performed on ten ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$) and six ($^{87}\text{Sr}/^{86}\text{Sr}$) whole-rock samples of gypsum and anhydrite, as representative of different sulphate lithofacies and diagenesis (Figs. 2–4 and Table 1).

Initially, all samples were evaluated petrographically to separate gypsum from anhydrite and pure fragments without non-sulphate phases (clay, carbonate and quartz). Elemental compositions of the samples were examined by XRF analyses. Microsampled powders were then prepared by drilling separated parts of samples with 1 mm diamond drill bits. The same powdered samples were used for sulphur, oxygen and strontium isotope analyses.

The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ analyses were carried out at the Mass Spectrometry Laboratory, Maria Curie-Skłodowska University in Lublin, Poland. For these analyses ca. 40 mg of each pow-

dered sample was dissolved in 100 ml of distilled water. The water was stirred from time to time during dissolution, which was extended up to 3 days. After dissolution of sulphates the solutes were filtered to small glass beakers. BaSO_4 was precipitated by means of the BaCl_2 solution acidified with HCl . The precipitate was washed by distilled water several times until disappearance of the chloride ion, tested by adding a few drops of 10% AgNO_3 solution to the decanted solution. The clean BaSO_4 residue was dried in small beakers in an oven at 100°C and then subjected to the procedures for quantitative extraction of sulphur and oxygen for isotopic analysis.

The isotopic compositions, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$, were analyzed by means of a dual inlet and triple collector mass spectrometer on SO_2 and CO_2 gases, respectively. SO_2 was extracted directly from BaSO_4 by the method developed in the Mass Spectrometry Laboratory in Lublin (Hałas and Szaran, 2001, 2004), whereas CO_2 was prepared by the method described by Mizutani (1971). In the last method a CO -to- CO_2 converter was modified by installing of 2 small magnets to enhance the discharge current. Typically 8 to 12 mg of BaSO_4 was used in each gas preparation. The reproducibility of both analyses in terms of standard deviation (SD) was 0.07‰. Delta values were normalized to the V-CDT and V-SMOW scales by analysis of the NBS-127 standard, for which $\delta^{34}\text{S} = +21.14\text{‰}$ and $\delta^{18}\text{O} = +9.30\text{‰}$ were assumed (Hałas and Szaran, 2001; Boschetti and Iacumin, 2005). The analytical precisions were 0.15‰ for both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$, and all values have been expressed as ‰ CDT and ‰ SMOW, respectively.

The strontium isotope compositions were analyzed at the Geochronology and Isotopic Geochemistry Laboratory, Univ-



Fig. 3. Selenitic gypsum partly replaced by nodular anhydrite

Borehole Pysznica U-19, depth 453.4 m



Fig. 4. Organic-rich claystone with anhydrite laminae and lenses composed of pseudomorphs after lenticular gypsum crystals

Borehole Ryszkowa Wola 7, depth 2410.5 m

ersidad Complutense de Madrid in Madrid. Previously weighed in Teflon® vials powdered samples of gypsum and anhydrite (25 mg) were dissolved in 8 ml of ultrapure Milli-Q (Millipore®) water (Lu *et al.*, 1997; Denison *et al.*, 1998; Jacobson *et al.*, 2005), through a period of 10 days at room temperature, shaking the vials once a day (Fuenlabrada *et al.*, 2001). The XRD results showed that the gypsum sample no. 1 (Table 1) had got some impurities of anhydrite. Therefore, the

dissolution method of this sample was slightly changed to eliminate the possible contamination in the final ratio. Taking into account that anhydrite is more soluble than gypsum in pure water at 25°C (Møller, 1988), 25 mg of powdered sample was dissolved in 8 ml of ultrapure water during two days, and then centrifuged for 10 minutes to eliminate the dissolved fraction and assuming that the total anhydrite was dissolved. Then ultrapure water was added again to the residue, in order to dissolve (through 10 days) the remaining gypsum sample. After that time, samples were centrifuged for 10 minutes, in order to separate the dissolved fraction from the residue. The dissolved fraction was heated at about 100°C, to reach a complete evaporation of the dissolution. The dry evaporated samples were dissolved in 2 ml of distilled and titrated 2.5N HCl at room temperature, or by means of an ultrasonic bath. After such preparation samples were ready to be passed through the chromatographic columns. For this internal protocol to separate strontium (Sr) from the rest of elements, cation exchange resin DOWEX 50W-X12 200–400 mesh was used (Strelow, 1960; Pankhurst and O’Nions, 1973). Previously, these chromatographic columns were calibrated to define the Sr fraction, and the volume of HCl 2.5N necessary to recover the maximum amount of this element free from rubidium traces. The Sr samples were collected in clean vials and dried at about 80°C. Dry strontium samples were dissolved in 1 ml of phosphoric acid (1M concentration), and the mixture was loaded over a simple tantalum filament (previously degassed).

The samples were introduced into the *Thermal Ionization Mass Spectrometer (TIMS) Micromass VG Sector-54* and analyzed using the standard method of measurement called dynamic multicollection, with five Faradays cups. Strontium analyses were corrected from possible ^{87}Rb interferences. The obtained $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized using the valor $^{88}\text{Sr}/^{86}\text{Sr} = 0.1194$ as a reference, in order to correct the mass fractionation in the sample through the total analysis time. NBS-987 was chosen as an isotopic standard of Sr to analyze at the same time with samples. This standard provided a correction factor that let us to eliminate or minimize possible troubles in the sample analysis. An average $^{87}\text{Sr}/^{86}\text{Sr}$ value (11 analysis of NBS-987) was 0.710223 (SD = 0.00003), which fitted quite well to the value 0.710253 (SD = 0.00004) obtained through 582 analysis of the same standard. The analytical error of the laboratory in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, referred to two standard deviations, was 0.01%.

RESULTS

All results of isotopic studies are summarized in Table 1. The $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values for analysed sulphate samples are cross-plotted in Figures 6 and 7, and a comparison of these values with previous data for marine sulphate deposits in the Carpathian Foredeep is shown in Figures 5 and 6.

The δ values are from +22.07 to +24.91‰ CDT for sulphur and from +11.96 to +13.63‰ SMOW for oxygen, and the average values are respectively +23.63‰ (SD = 0.82) and +12.74‰ (SD = 0.39) (Table 1). Both isotopic compositions are positively correlated, showing the $\delta^{18}\text{O}$ values in a smaller

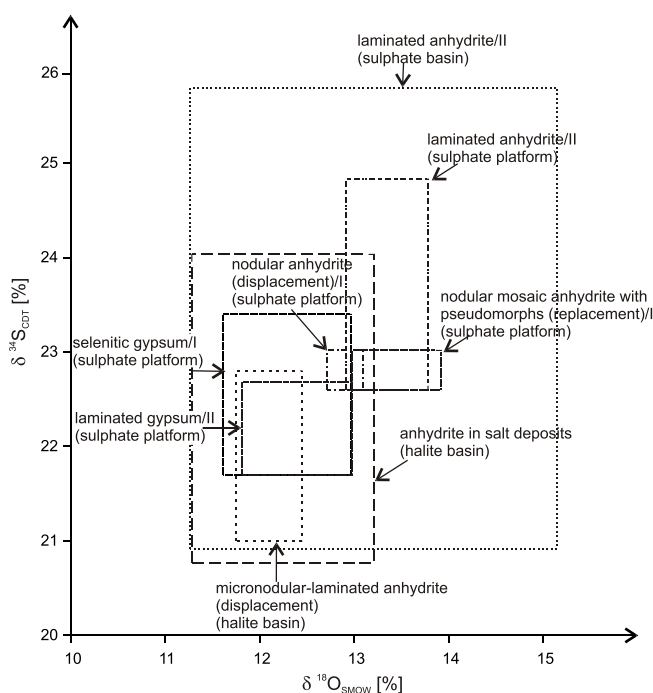


Fig. 5. Oxygen and sulphur isotope composition of Badenian sulphates (gypsum and anhydrite) in the Carpathian Foredeep (based on data from: Bukowski and Szaran, 1997; Kasprzyk, 1997, 2003; Peryt *et al.*, 1998; Cendón *et al.*, 2004)

I — lower member; II — upper member

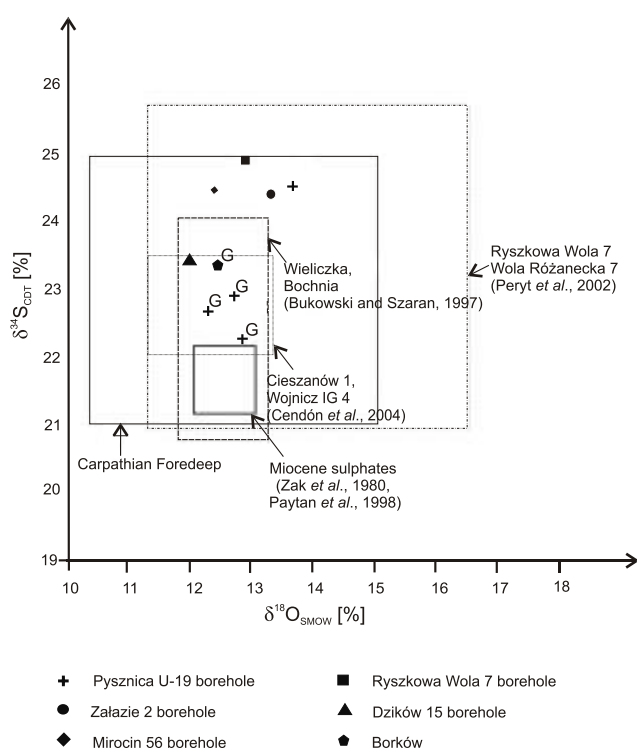


Fig. 6. Plot of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values in studied gypsum and anhydrite samples

Isotopic compositions of Miocene marine sulphates (thick solid line; after Zak *et al.*, 1980; Paytan *et al.*, 1998) and Badenian sulphate deposits in the Carpathian Foredeep (after Bukowski and Szaran, 1997; Kasprzyk, 2003; Peryt *et al.*, 2002; Cendón *et al.*, 2004) are also shown; indicated (G) are gypsum samples and the others are anhydrite

range of variation than $\delta^{34}\text{S}$ (Fig. 6). It is worth noting that the average δ values for anhydrite samples are higher (by about 2‰ for sulphur and 0.5‰ for oxygen) than for gypsum. Overall, the results coincide with values expected for the Miocene sulphates of the marine origin only for the oxygen (Zak *et al.*, 1980; Paytan *et al.*, 1998) (Fig. 6).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of gypsum and anhydrite samples range from 0.708915 to 0.716329 (Table 1). All samples yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.711577 (SD = 0.002802). The gypsum samples have a mean $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.709036; $n = 2$) that is largely lower than the mean $^{87}\text{Sr}/^{86}\text{Sr}$ value of the anhydrite samples (0.712847; $n = 4$). The $\delta^{34}\text{S}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ relationships of gypsum and anhydrite are illustrated in Figure 7. The $^{87}\text{Sr}/^{86}\text{Sr}$ for anhydrite samples shows a wide range of values (from 0.709581 to 0.716329), while gypsum samples have $^{87}\text{Sr}/^{86}\text{Sr}$ values largely lower (0.708915 and 0.709157).

INTERPRETATION AND DISCUSSION

S AND O ISOTOPE COMPOSITION

The sulphur and oxygen isotope compositions of studied gypsum and anhydrite samples vary within relatively narrow ranges. Overall, the results correspond well to the previously reported isotopic composition of Badenian sulphate (gypsum and anhydrite) deposits in the Carpathian Foredeep (e.g., Kasprzyk, 1997, 2003; Peryt *et al.*, 2002 and references therein) (Figs. 5 and 6). Recently, Cendón *et al.* (2004) argued that sulphate isotope values are not by themselves indicative of the marine or non-marine origin of the sulphate and stressed the importance of major continental inputs and ongoing intrabasinal recycling processes in formation of Badenian sulphate deposits. Peryt *et al.* (2002) stressed that there was a lithological control on the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values. Those authors, however, did not differentiate between the gypsum and anhydrite lithologies, and the palaeogeographic location of studied samples. There are some regular changes between samples studied in our work, which show that δ values for the gypsum samples are distinctly lower in sulphur and slightly lower in oxygen when compared to anhydrite samples. Our results indicate that there is a distinct lithofacies (gypsum–anhydrite) and palaeogeographic (basin margin–basin centre) control on sulphur and oxygen isotope compositions, showing an increase of δ values for samples coming from more basinal settings (Table 1 and Fig. 2).

Most of δ values are located far from the marine field ($\delta^{34}\text{S} = +21.65 \pm 0.5\text{‰}$, $\delta^{18}\text{O} = +12.5 \pm 0.5\text{‰}$; Zak *et al.*, 1980; Paytan *et al.*, 1998) indicated by the box in Figure 6. Hence the sulphate with elevated δ values must either arise from the addition of dissolved sulphate to the basin from a non-marine source or reflect an isotope fractionation processes within the basin, such as dissolution of the previous evaporites and reprecipitation of the sulphate (a process termed “recycling”), or microbially mediated sulphate reduction. These geochemical factors involving the sulphate isotope compositions are discussed below.

Variations in δ values may have resulted from a non-marine contribution to the basin. Dissolved sulphates in continental

(e.g. riverine) waters are usually derived from the dissolution of former evaporite deposits, the oxidation of pyrite weathered from shales or igneous rocks, a magmatic source through thermal waters, and also volcanic related inputs. Continental waters are generally depleted in ^{34}S and ^{18}O compared to seawater (Lu and Meyers, 2003; Palmer *et al.*, 2004). Isotopic compositions of both elements can be very variable, showing common values -5 to $+5\text{‰}$ for $\delta^{34}\text{S}$ and -10 to $+5\text{‰}$ for $\delta^{18}\text{O}$ (Nielsen, 1972). However, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of marine gypsum are insensitive to minor non-marine contributions, because seawater and seawater-evaporated brines have much higher SO_4^{2-} concentration than most freshwaters (Lu and Meyers, 2003; Palmer *et al.*, 2004). For the Badenian evaporite basin, geochemical studies and model calculations of the basin evolution suggest a major inflow of continental waters, up to 65–70%, with a marine input being less than 30% during halite precipitation (Cendón *et al.*, 2004).

The isotopically heavy sulphate may come from recycling of the former evaporites by continental waters, as previously suggested by Peryt *et al.* (2002) and Cendón *et al.* (2004) for Badenian sulphates. Sedimentological and geochemical data indicate recycling of evaporites throughout most of the evaporite deposition, but especially during deposition of allochthonous sulphate facies. Our results show that the enrichment in ^{34}S for some anhydrite samples is higher than expected from the simple dissolution-reprecipitation of sulphate, assuming that the Miocene gypsum (or anhydrite) was the original sulphate dissolved (Cendón *et al.*, 2004). Therefore, the high δ values probably imply either multiple cycles of dissolution and reprecipitation of sulphate or, alternatively, anoxic conditions favouring sulphate-reducing bacterial activity in depositional environments. Peryt (2006) concluded that deposition of halite in the basin centre preceded the autochthonous sulphate deposition (lower member) in the marginal basin, while that of allochthonous sulphate facies (upper member) was roughly coeval in the entire evaporite basin. Thus, the high $\delta^{34}\text{S}$ values of the basinal anhydrite samples illustrated in Figure 6 indicate that restricted conditions very likely occurred in the basin centre during redeposition of evaporites.

It is more difficult to establish, however, whether enriched $\delta^{34}\text{S}$ compositions reflect basin-scale or local compositional evolution of parent brines. Holser (1977) suggested that large brine-accumulating basins with a limited connection to the open sea could evolve highly enriched S-isotope compositions, perhaps *via* biogenic sulphate reduction and pyrite deposition within euxinic basinal brines, or *via* “normal” sulphate reduction in a basin that is sulphate limited from large-scale deposition of evaporites. In the history of the Badenian salinity crisis, recently summarized by Peryt (2006), the evaporite deposition commenced in the deepest part of the basin in density-stratified brines, and was possibly preceded by the syndepositional sulphate nodule growth in the underlying organic-rich siliciclastic deposits. It is suggested, that the occurrence of pyritic and organic-rich deposition as well as pyrite aggregate pseudomorphs after gypsum in basinal settings of the Carpathian Foredeep Basin, coeval with evaporite deposition (Kasprzyk and Ortí, 1998; Kasprzyk, 2003, 2006; Oszczyk *et al.*, 2005), indicates that sulphate reduction was active in a restricted, and therefore sulphate-limited basin. Thus, the ele-

vated $\delta^{34}\text{S}$ values as observed by us could be attributed to closed system conditions with an important role played by bacterial sulphate reduction in the basin partly separated from the open sea.

On the basis of our study it is suggested that either sulphate reduction or non-marine contribution by intrabasinal evaporite recycling, or both, could have a great impact on the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values before or during gypsum deposition in the Carpathian Foredeep Basin, and resulted in variation of isotopic compositions of Badenian sulphate deposits.

There is no sulphur and oxygen isotope fractionation during the gypsum-to-anhydrite transformation (Pierre, 1988; Utrilla *et al.*, 1992; Kasprzyk, 2003). Thus, the anhydrite (considered to be a diagenetic product) still preserves the isotopic signature of the original (depositional) gypsum, unless bacterial reduction has taken place. The occurrence of pyrite pseudomorphs after gypsum crystals in Badenian anhydrites argues for early (syndepositional and early diagenetic) stages of redox processes active in the evaporite basin (Kasprzyk, 2005). Therefore, the isotopic differentiation between gypsum and anhydrite recorded by us seems to reflect a lateral compositional evolution of parent waters during sulphate deposition in the Carpathian Foredeep Basin.

Sr ISOTOPE COMPOSITION

The Sr isotope compositions of evaporites reflect the composition of mother brines, which is a response to changing inputs and sources of dissolved strontium, together with possible interactions between the brines and rocks within the evaporite basin (Brass, 1976; Kah *et al.*, 2001; Lu and Meyers, 2003; Palmer *et al.*, 2004). Sr isotope studies are particularly useful in monitoring the continental inputs into the marine basin. The Sr isotope composition of Neogene seawater is well established (e.g., Koepnick *et al.*, 1985; Hodell *et al.*, 1991; McArthur *et al.*, 2001), thus, the $^{87}\text{Sr}/^{86}\text{Sr}$ of Badenian seawater is well known (0.708698–0.708817). There are no available Sr isotope data for non-marine fluids (river water or groundwater) in the study area. In general, non-marine waters are characterized by higher $^{87}\text{Sr}/^{86}\text{Sr}$ values and lower Sr concentrations compared to values of normal Miocene seawater (Palmer and Edmond, 1989; Lu and Meyers, 2003). Some geochemical data for halites and model calculations for the Badenian basin evolution record a major continental source for solutes, seawater being a minor inflow (less than 30%) to the basin during the evaporite deposition (Cendón *et al.*, 2004 and references therein). Our interest is whether the Sr isotope data record this non-marine contribution to the evaporite basin of the Carpathian Foredeep.

Most studied sulphate samples (both gypsum and anhydrite) show $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.708915–0.716329; Table 1) that are higher to much higher than contemporaneous Badenian seawater (e.g., Hodell *et al.*, 1991; McArthur *et al.*, 2001), and thus demonstrate that these sulphates were formed from brines with a significant component of non-marine Sr. Lu and Meyers (2003) stressed that a contribution of non-marine water could have been masked by the marine $^{87}\text{Sr}/^{86}\text{Sr}$ signature because of a much higher Sr concentration in the

brine than in the continental waters. In spite of this reason, our results are unequivocal and point to a contribution of highly radiogenic strontium to the basin.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of two gypsum samples (no. 1 and 3 in Table 1) are close to the Badenian seawater Sr isotope values (0.708698–0.708817; Hodell *et al.*, 1991), suggesting a dominantly marine origin. However anhydrite samples of the upper (clastic) member have more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the gypsum samples, strongly indicating radiogenic strontium non-marine contribution, and also trend towards higher $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ (Fig. 7). It is possible that mixing of marine and continental waters was responsible for these relationships. Indeed, the mixing of continental and marine waters played a major role in the variation of strontium isotopes in some evaporite deposits (Denison *et al.*, 1998; Playa *et al.*, 2000; Lu and Meyers, 2003; Palmer *et al.*, 2004).

Sedimentary and geochemical evidence imply that the water level fluctuated significantly during the sulphate deposition in the Badenian basin, which in turn was interrupted by influxes of freshwater (e.g. Kasprzyk, 2003; Cendón *et al.*, 2004; Babel, 2005). The redeposition of evaporites, especially during sedimentation of the upper member clastic deposits, was important, and although parent brines were marine in origin, they were subject to significant inflows of meteoric waters (Cendón *et al.*, 2004; Peryt, 2006). The scatter of strontium isotope results in the sulphate samples is interpreted here to reflect the contribution of meteoric strontium to the basin. Thus, the Sr isotope data confirm the above interpretation suggesting that Badenian sulphates originated from marine brines with a significant and variable contribution of meteoric waters.

The results of this study show Sr isotopic differences between the sedimentary (gypsum) and diagenetic (anhydrite) lithofacies (Fig. 7). The latter are highly radiogenic, suggesting that before or during anhydritization of gypsum interstitial brines underwent Sr isotope exchange with other circulating fluids. The high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in anhydrite samples can be interpreted as resulted from the mixing of fluids of two different isotopic signatures, i.e., marine waters and continental waters, during sulphate deposition and diagenesis. The mete-

oric contribution is documented by a presence of siliciclastic impurities and interbeds in anhydrite successions (Fig. 2). An influence of interbedded siliciclastic deposits as sources of highly radiogenic strontium could be important by simple mixing and interactions between the brines and rocks (Denison, pers. comm., 2007). Thus, the different strontium isotope compositions of gypsum and anhydrite seem to reflect two different hydrological provenances of sulphate formation in the Badenian basin.

Some authors suggested an important influence of the Carpathian orogen on the evaporite deposition by promoting the expulsion of buried brines from the flysch sediments during Carpathian overthrusting (Liszkowski, 1989; Eastoe and Peryt, 1999; Peryt, 2006). Although, it is difficult to establish the time relations of these processes and the anhydritization of detrital gypsum deposits, the both could affect the isotopic compositions of the basinal sulphate facies close to the Carpathian front.

CONCLUSIONS

Isotopic signatures of Badenian sulphates show that marine water was the dominant source of sulphate and Sr, but that strong perturbations from the original seawater resulted from the major contributions of non-marine waters and sulphate reduction reactions in depositional settings.

Variations in isotopic signatures of sulphate samples ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) reflect active recycling and biogeochemical (bacterial) processes during sulphate deposition and inflows of continental waters enriched in isotopically light sulphur and radiogenic strontium compounds into the basin, and therefore may be related to environmental changes along with an episodic isolation and refreshment of the basin, most probably controlled by tectonic and eustatic changes.

The results also suggest that gypsum (sedimentary facies) and anhydrite (diagenetic facies) were formed in different hydrological settings in a basin affected by important and variable

non-marine (riverine, groundwater) inputs. Gypsum was formed from brines marine in origin that underwent an important inflow of continental waters and local bacterial sulphate reduction. Anhydrite isotopic signatures reflect highly radiogenic non-marine inputs to the basin, most likely related to mixing from terrigenous sources or expulsion of buried brines caused by the Carpathian orogeny.

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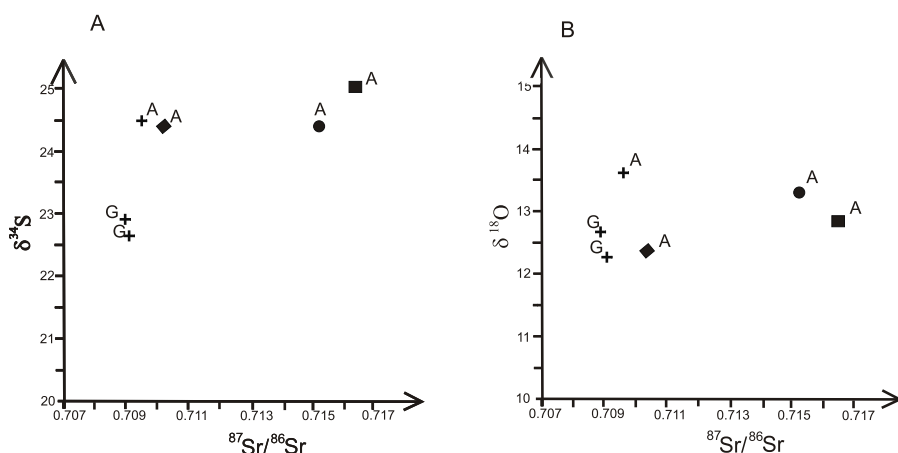


Fig. 7. Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ (A) and $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ (B) of sulphate deposits: gypsum (G) and anhydrite (A)

Sample symbols explained in Figure 6

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REFERENCES

- ANDREYEVA-GRIGOROVICH A. S., OSZCZYPKO N., SAVITSKAYA N. A., ŚLĄCZKA A. and TROFIMOVICH N. A. (2003) — Correlation of Late Badenian salts of the Wieliczka, Bochnia and Kalush areas (Polish and Ukrainian Carpathian Foredeep). *Ann. Soc. Geol. Pol.*, **73**: 67–89.
- BĄBEL M. (1999) — Facies and depositional environments of the Nida Gypsum deposits (Middle Miocene, Carpathian Foredeep, southern Poland). *Geol. Quart.*, **43** (4): 405–428.
- BĄBEL M. (2005) — Selenite-gypsum microbialite facies and sedimentary evolution of the Badenian evaporite basin of the northern Carpathian Foredeep. *Acta Geol. Pol.*, **55** (2): 187–210.
- BOSCHETTI T. and IACUMIN P. (2005) — Continuous-flow $\delta^{18}\text{O}$ measurements: new approach to standardization, high-temperature thermodynamic and sulfate analysis. *Rapid Comm. Mass Spectrom.*, **19**: 3007–3014.
- BRASS G. W. (1976) — The variation of the marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratio during Phanerozoic time: interpretation using a flux model. *Geochim. Cosmochim. Acta*, **40**: 721–730.
- BUKOWSKI K. and SZARAN J. (1997) — Zawartość izotopów tlenu i siarki w anhydrytach z serii solonośnej Wieliczki i Bochni. *Prz. Geol.*, **45** (8): 81–818.
- CENDÓN D. I., PERYT T. M., AYORA C., PUEYO J. J. and TABERNER C. (2004) — The importance of recycling processes in the Middle Miocene Badenian evaporite basin (Carpathian foredeep): palaeoenvironmental implications. *Palaeogeogr. Palaeoclimat. Palaeoecol.*, **212**: 141–158.
- DENISON R. E., KIRKLAND D. W. and EVANS R. (1998) — Using strontium isotopes to determine the age and origin of gypsum and anhydrite beds. *J. Geol.*, **108**: 1–17.
- DUDEK K., BUKOWSKI K. and WIEWIÓRKA J. (2004) — Datowania radiometryczne badeńskich osadów piroklastycznych z okolic Wieliczki i Bochni. In: *Datowanie minerałów i skał* (eds. M. Michalik, K. Jacher-Śliwczynska, M. Skiba and J. Michalik): 19–26. VIII Ogólnopolska Sesja Nauk.
- EASTOE C. J. and PERYT T. (1999) — Stable chlorine isotope evidence for non-marine chloride in Badenian evaporites, Carpathian mountain region. *Terra Nova*, **11**: 118–123.
- FUENLABRADA J. M. and GALINDO C. (2001) — Comportamiento de la relación $^{87}\text{Sr}/^{86}\text{Sr}$ en disoluciones de carbonatos impuros en función de la concentración ácida y en disoluciones de sulfatos en función del tiempo. III Congreso Ibérico de Geoquímica: 591–595.
- GARLICKI A. (1979) — Sedimentation of Miocene salts in Poland (in Polish with English summary). *Pr. Geol.*, **119**: 1–66.
- HAŁAS S. and SZARAN J. (2001) — Improved thermal decomposition of sulfates to SO_2 and mass spectrometric determination of IAEA SO-5, IAEA SO-6 and NBS-127 sulfate standards. *Rapid Comm. Mass Spectrom.*, **15**: 1618–1620.
- HAŁAS S. and SZARAN J. (2004) — Use of $\text{Cu}_2\text{O}-\text{NaPO}_3$ mixtures for SO_2 extraction from BaSO_4 for sulphur isotope analysis. *Isotopes Environ. Health Stud.*, **40**: 229–231.
- HAŁAS S., JASIONOWSKI M. and PERYT T. (1996) — Isotopic anomaly in the Badenian gypsum of the Nida River Valley (southern Poland) (in Polish with English summary). *Prz. Geol.*, **44** (10): 1054–1056.
- HARDIE L. A. (1984) — Evaporites: marine or non-marine? *Am. J. Sci.*, **284**: 193–240.
- HODELL D. A., MUELLER P. A. and GARRIDO J. R. (1991) — Variations in the strontium isotopic composition of seawater during the Neogene. *Geology*, **19**: 24–27.
- HOLSER W. T. (1977) — Catastrophic chemical events in the history of the ocean. *Nature*, **267**: 403–408.
- HORITA J., ZIMMERMANN H. and HOLLAND H. D. (2002) — Chemical evolution of seawater during the Phanerozoic: implications from the record of marine evaporites. *Geochim. Cosmochim. Acta*, **66**: 3733–3756.
- JACOBSON A. D. and WASSERBURG G. J. (2005) — Anhydrite and the Sr isotope evolution of groundwater in a carbonate aquifer. *Chem. Geol.*, **214**: 331–350.
- KAHL L. C., LYONS T. W. and CHESLEY J. T. (2001) — Geochemistry of a 1.2 Ga carbonate-evaporite succession, northern Baffin and Bylot Islands: implications for Mesoproterozoic marine evolution. *Precamb. Res.*, **111**: 203–234.
- KASPRZYK A. (1993) — Lithofacies and sedimentology of the Badenian (Middle Miocene) gypsum in the northern part of the Carpathian Foredeep, southern Poland. *Ann. Soc. Geol. Pol.*, **63**: 33–84.
- KASPRZYK A. (1997) — Oxygen and sulphur isotope composition of Badenian (Middle Miocene) gypsum deposits in southern Poland: a preliminary study. *Geol. Quart.*, **41** (1): 53–60.
- KASPRZYK A. (1999) — Sedimentary evolution of Badenian (Middle Miocene) gypsum deposits in the northern Carpathian Foredeep. *Geol. Quart.*, **43** (4): 449–465.
- KASPRZYK A. (2003) — Sedimentological and diagenetic patterns of anhydrite deposits in the Badenian evaporite basin of the Carpathian Foredeep, southern Poland. *Sedim. Geol.*, **158**: 167–194.
- KASPRZYK A. (2005) — Diagenetic alteration of Badenian sulphate deposits in the Carpathian Foredeep Basin, Southern Poland: processes and their succession. *Geol. Quart.*, **49** (3): 305–316.
- KASPRZYK A. and ORTÍ F. (1998) — Palaeogeographic and burial controls on anhydrite genesis: the Badenian basin in the Carpathian Foredeep (southern Poland, western Ukraine). *Sedimentology*, **45**: 889–907.
- KOEPNICK R. B., BURKE W. H., DENISON R. E., HETHERINGTON E. A., NELSON H. F., OTTO J. B. and WAITE L. E. (1985) — Construction of the Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve for the Cenozoic and Cretaceous: supporting data. *Chem. Geol.*, **58**: 55–81.
- KUBICA B. (1992) — Lithofacial development of the Badenian chemical sediments in the northern part of the Carpathian Foredeep (in Polish with English summary). *Pr. Państw. Inst. Geol.*, **133**: 1–64.
- LISZKOWSKI J. (1989) — Organiczno-descensyjny model genetyczny miocenijskich formacji solinarnych regionu karpaccyjskiego wschodnich obszarów Centralnej Paratetydy. *Pr. Nauk. Uniw. Śl.*, **1019**: 1–102.
- LU F. H. and MEYERS W. J. (2003) — Sr, S and O_{SO_4} isotopes and the depositional environments of the Upper Miocene evaporites, Spain. *J. Sedim. Res.*, **73**: 444–450.
- LU F. H., MEYERS W. J. and SCHOONEN M. A. (1997) — Trace and minor element analyses on gypsum: an experimental study. *Chem. Geol.*, **142**: 1–10.
- LU F. H., MEYERS W. J. and SCHOONEN M. A. (2001) — S and O (SO_4) isotopes, simultaneous modeling, and environmental significance of the Nijar messinian gypsum, Spain. *Geochim. Cosmochim. Acta*, **65** (18): 3081–3092.
- McARTHUR J. M., HOWARTH R. J. and BAILEY T. R. (2001) — Strontium isotope stratigraphy: LOWESS version 3: best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. *J. Geol.*, **109**: 155–170.
- MIZUTANI Y. (1971) — An improvement in the carbon — reduction method for the isotopic analysis of sulfates. *Geochem. J.*, **5**: 69–77.

- MØLLER N. (1988) — The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na-Ca-Cl-SO₄-H₂O system, to high temperature and concentration. *Geochim. Cosmochim. Acta*, **52**: 821–837.
- NIELSEN H. (1972) — Sulphur isotopes and the formation of evaporite deposits. In: *Geology of Saline Deposits* (ed. G. Richter-Bernburg). *Earth Sc.*, **7**: 91–102.
- OSZCZYPKO N., KRZYWIEC P., POPADYUK I. and PERYT T. (2005) — Carpathian Foredeep Basin (Poland and Ukraine) — its sedimentary and Geodynamic Evolution. In: *The Carpathians and Their Foreland: Geology and hydrocarbon resources* (eds. J. Golonka and F. J. Picha). *AAPG Mem.*, **84**: 293–350.
- PALMER M. R. and EDMOND J. M. (1989) — The strontium isotope budget of the modern ocean. *Earth Planet. Sc. Lett.*, **92**: 11–26.
- PALMER M. R., HELVACÍ C. and FALLICK A. (2004) — Sulphur, sulphate oxygen and strontium isotope composition of Cenozoic Turkish evaporites. *Chem. Geol.*, **209**: 341–356.
- PANKHURST R. J. and O'NIONS R. K. (1973) — Determination of Rb/Sr and ⁸⁷Sr/⁸⁶Sr ratios of some standard rocks and evaluation of X-Ray fluorescence spectrometry in Rb-Sr geochemistry. *Chem. Geol.*, **12** (2): 127–136.
- PAYTAN A., KASTNER M., CAMPBELL D. and THIEMENS M. H. (1998) — Sulphur isotopic composition of Cenozoic seawater sulphate. *Science*, **282**: 1459–1462.
- PERYT T. M. (2006) — The beginning, development and termination of the Middle Miocene Badenian salinity crisis in Central Paratethys. *Sedim. Geol.*, **188–189**: 379–396.
- PERYT T. M., PERYT D., SZARAN J., HAŁAS S. and JASIONOWSKI M. (1998) — Middle Miocene Badenian anhydrite horizon in the Ryszkowa Wola 7 borehole (in Polish with English summary). *Biul. Państw. Inst. Geol.*, **379**: 61–78.
- PERYT T. M., SZARAN J., JASIONOWSKI M., HAŁAS S., PERYT D., POBEREZHSKYY A., KAROLI S. and WÓJTOWICZ A. (2002) — S and O isotope composition of the Badenian (Middle Miocene) sulphates in the Carpathian Foredeep. *Geol. Carpath.*, **53** (6): 391–398.
- PIERRE C. (1988) — Applications of stable isotope geochemistry to the study of evaporites. In: *Evaporites and Hydrocarbons* (ed. B.C. Schreiber): 300–344. Columbia Univ. Press, New York.
- PLAYA E., ORTÍ F. and ROSELL L. (2000) — Marine to non-marine sedimentation in the upper Miocene evaporites of the Eastern Betics, SE Spain: sedimentological and geochemical evidence. *Sedim. Geol.*, **133**: 135–166.
- ROSELL L., ORTÍ F., KASPRZYK A., PLAYÁ E. and PERYT T. (1998) — Strontium geochemistry of Miocene primary gypsum: Messinian of SE Spain and Sicily and Badenian of Poland. *J. Sedim. Res.*, **68**: 63–79.
- SCHREIBER B. C. and EL TABAKH M. (2000) — Deposition and early alteration of evaporites. *Sedimentology*, **47**: 215–238.
- STRELOW F. W. (1960) — An ion exchange selectivity scale of cations based on equilibrium distribution coefficients. *An. Chem.*, **32**: 1185–1188.
- UTRILLA R., PIERRE C., ORTÍ F. and PUEYO J. J. (1992) — Oxygen and sulphur isotope compositions as indicators of the origin of Mesozoic and Cenozoic evaporites from Spain. *Chem. Geol.*, **102**: 229–244.
- ZAK I., SAKAI H. and KAPLAN I. R. (1980) — Factors controlling the ¹⁸O/¹⁶O and ³⁴S/³²S isotope ratios of ocean sulfate evaporites and interstitial sulfates from modern deep-sea sediments. In: *Isotope Marine Chemistry*: 339–373. Uchida Rokakuho, Tokyo.